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RELATION OF INTERFACIAL ENERGY TO THE MOLECULAR STRUCTURE OF ORGANIC COMPOUNDS

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BY

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STUDIES ON ELECTROKINETIC POTENTIALS. V. INTERFACIAL ENERGY AND THE MOLECULAR STRUCTURE OF ORGANIC COMPOUNDS. I. ELECTROKINETIC POTENTIALS AT CELLULOSE-ORGANIC LIQUID INTERFACES*

BY WILLIAM McKINLEY MARTIN** AND ROSS AIKEN GORTNER

Introduction

In its simplest aspects, surface or interfacial energy probably arises from the unbalanced electrical environment of the molecules bounding the interfaces of simple or polyphase systems.

With the introduction of the electrogenetic concept of matter, the modern trend of thought visualizes chemical compounds as dynamic entities, the unreactive or stable molecule being the exception rather than the rule. In accordance with this view, the electrical properties of molecules are very greatly influenced by the environmental conditons of each molecule, or by its electrical atmosphere. If the electrical atmosphere of a molecule is such as to leave its residual electrical affinities uncompensated or unneutralized, these uncompensated forces may be thought of as the "free" or "external" energy of the molecule. Since the reactivity or instability of the molecules of a system is, in reality, the tendency of that system to reduce its free energy to a minimum, it follows that the reactivity of reacting molecules is a measure of their free energies. Obviously the converse is also true. With this concept, it follows that a change in the environment of a molecule which alters its electrical balance with a consequent change in its free energy will result in a change in its reactivity.

In homogeneous systems of either pure liquids or solutions, the electrical forces acting upon a given molecule are presumably equal in all directions, but may vary according to the so-called cohesive or adhesive forces of adjacent molecules, hence there will be no orientation. However, the density of the electrical atmosphere surrounding each molecule or ion, in the case of solutions, will change with concentration. An attempt to evaluate this change has been made recently in the case of inorganic electrolytes, and the term, "activity coefficient," has been introduced.

In heterogeneous systems, however, the boundary molecules of the disperse phase will have uncompensated forces at the interface. These uncompensated or residual forces probably function in attracting molecules of the

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continuous phase, with a consequent reduction of free energy, and an orientation of the molecules at the interface. Here again, there is probably a change in the electrokinetics of the molecules so oriented, brought about by the system reducing its free energy content to a minimum. The adsorbed or oriented molecules may be visualized as having their electrical balance destroyed with a consequent increase in the uncompensated or residual forces in the opposite "end" of the molecules. From an electrokinetic point of view, such molecules may be looked upon as being "distorted" or unbalanced with respect to their normal state in homogeneous systems, and are undoubtedly rendered more reactive through a shifting in their energy equilibrium.

Another factor operative in surface catalysts is the concentrating of substances at the interface. That this is in accordance with observed facts is indicated by the increase in rate of chemical reactions by contact catalysts and by the so-called "wall reaction" effects, over that which would be expected from the mass action law, when considered in relation to the concentrations of the reacting substances in the homogeneous phase.

In biological systems where the concentrations of the reacting substances are relatively low, specific enzymes function in bringing about chemical reactions, many of which are utterly impossible of accomplishment by any known laboratory methods. All enzymes, as far as we know, possess one common property, in that they are colloidal in nature, and undoubtedly involve surface or interfacial energy changes in their catalytic action.

Although the nature of the specificity of enzyme action is not yet understood, the more advanced thinkers in this field, notably, Oppenheimer[1] and Willstätter[2] are agreed that enzymes are colloidal aggregates having special reactive groups which combine with, or possess an affinity for, definite groupings in the substrate; and that enzyme action is determined in part by the affinity of the active group for the substrate, and in part by the colloidal nature of the entire aggregate. Willstätter, especially, has secured considerable experimental evidence in support of this view.

It seems then that it would not be a stretch of imagination to associate the generally recognized phenomenon of surface catalysis with the colloidality of enzymes. Undoubtedly the anomalous chemical activity induced by these colloidal materials in plant and animal cells can be explained, at least in part, by the concentrating of the reacting substance at interfaces, and by a subsequent orientation and distortion of the electrical fields of the molecules. It follows then that, since all chemical reactions are really energy transformations, interfaces are the loci where the magnitude of the free energy of molecules is intermediate between that of the reacting substances and the reaction products, the real catalytic effect being an "electrical distortion" of the molecules oriented at the boundary of the two phases.

Since the most characteristic property of protoplasm is its colloidality, one may look upon a living plant or animal cell as a miniature chemical laboratory, where innumerable anabolic and catabolic reactions go forward

[1] Oppenheimer: "Die Fermente und ihre Wirkungen", Vol. I (1925).

[2] Willstätter, Grasser, and Kuhn: Z. physiol. Chem., 123, 45 (1922).

simultaneously, the equilibrium of each reaction being shifted in either direction according to the energy relations at the interfaces, which relations are in turn regulated by changes in the concentration of the substances composing each particular phase.

Indirectly, there is considerable evidence in support of the view that surface energy is in some way connected with the anomalous reactivity of substances in biological systems, and the synthesis of organic compounds (using "organic" in its original sense) is catalyzed through changes in the electrical properties of molecules oriented at interfaces, and further that surface phenomena are concerned in the absorption and transformation of radiant energy and in the selective permeability of biological membranes.

Historical

That a difference does exist between the electrical properties of adsorbed molecules and similar ones in the interior of a phase, is shown by the difference in electrical potential between the molecules in these two situations. This potential difference was named electrokinetic potential by Freundlich.[3] Kruyt,[4] and Briggs[5] have also contributed much to the theory of electrokinetic phenomena in the way of experimental work and in the development of mathematical formulae. Briggs,[5] in the earlier papers of this series, has developed the streaming-potential method described by Kruyt[4] and Freundlich,[3] using diaphragms of cellulose, quartz, and proteins adsorbed on quartz instead of the capillary glass tubes used in the experiments of Kruyt and Freundlich.

The theoretical aspects of the problem, as well as the development of the mathematical formula expressing numerically the electrokinetic potential from the observed streaming-potential, have been discussed by Briggs[5] and Gortner[6] and will, therefore, be omitted from the present discussion. The work of Briggs was devoted mainly to studies on the ζ-potential of cellulose in aqueous solutions of inorganic salts and on the effects of acids, bases, and salts on the surface-electrical properties of proteins. Without attempting to review the results secured by Briggs, it will suffice to say that his studies opened up an entirely new field for the application of streaming-potential methods, in that he devised a method for the measurement of the interfacial potential of biological materials.

All of the streaming-potential measurements, aside from those of Briggs have been carried out by streaming water and aqueous solutions through capillary glass or quartz tubes. Up to the present, the ζ-potential values for non-aqueous systems involving pure organic liquids have apparently not been determined.

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[3] *Cf.* Freundlich and Rona: Sitz. preuss. Akad. Wiss., **20**, 397 (1920); Freundlich: "Colloid and Capillary Chemistry" (1926); Freundlich: "New Conceptions in Colloidal Chemistry" (1927).

[4] Kruyt: Kolloid-Z., **22**, 81 (1918); *cf.* also Kruyt and van der Willigen: **45**, 307 (1928).

[5] Briggs: J. Phys. Chem., **32**, 641 (1928); J. Am. Chem. Soc., **50**, 2358 (1928); J. Phys. Chem., **32**, 1646 (1928); Colloid Symposium Monograph, **6**, 41 (1929).

[6] Gortner: "Outlines of Biochemistry" (1929).

The Dorn[7] effect or "falling-potential," involving non-aqueous systems, was studied, however, by Stock[8] by dropping pulverized quartz through two-meter columns of diethylether and toluene and measuring the difference in potential between the top and bottom layers. Other studies bearing indirectly on the electrokinetic effects of non-aqueous systems were carried out by Strickler and Mathews,[9] in which they measured the rate of electro-endosmose of organic liquids through filter paper diaphragms.

Experimental

The Problem.—The object of the present investigation is to study the interfacial energy relations of solid-liquid systems of known composition, with special reference to the molecular structure of the phases concerned, and, if possible, to throw some light upon the dynamics of the molecules oriented at the liquid-solid interfaces. By confining the initial studies to pure compounds, unknown factors are obviously reduced to a minimum, while at the same time it is hoped that the information so obtained will open up some new leads which may be applied toward the solution of the more complex problems in biology.

The Method.—The value for the ζ-potential of a solid-liquid interface is calculated from the formula,

$$\zeta = \frac{4\pi\eta H\kappa_s}{P\epsilon},$$

where η = the coefficient of viscosity of the liquid, H = the observed electromotive force produced by streaming the liquid through a diaphragm of the solid, κ_s = the specific electrical conductivity of the diaphragm with the liquid in it, P = the hydrostatic pressure causing the liquid to stream through the diaphragm, and ϵ = the dielectric constant of the liquid in the diaphragm, all values being in c.g.s. units.

In the present investigation the values for η and ϵ have been taken from published tables. The values to be determined experimentally, then, are: electromotive force, the hydrostatic pressure of the streaming-liquid, and the specific electrical conductivity of the liquid in the diaphragm.

The streaming-potential method used in making these measurements was a modification of that employed by Briggs. He used aqueous solutions, the components of which were relatively inexpensive, and consequently the dimensions and arrangements of the streaming-cell of his apparatus were such as to require a comparatively large volume of liquid. Since some of the chemically pure organic liquids were very expensive, it was necessary to modify the streaming-cell and its accompanying parts, so as to reduce to a minimum the quantity of materials required for a determination.

In addition, some of the organic liquids were quite hygroscopic, and it was therefore necessary to design the apparatus so as to protect them against the absorption of moisture from the compressed air and from the atmosphere.

[7] Dorn: Wied. Ann., 9, 513; 10, 46 (1880).

[8] Stock: Anzeiger Akad. Wiss. Krakau, 1914A, 95.

[9] Strickler and Mathews: J. Am. Chem. Soc., 44, 1647 (1922).

Precautions were also taken to prevent the liquids from absorbing carbon dioxide by removing it from the air coming in contact with them. The working details of the apparatus used are shown in Figs. 1 and 2, the description of the parts being as follows: (A) compressed air tank, (B) Wheatstone bridge, (Ba) two 45-volt radio B batteries (90 volts), (Ba_1) storage battery as source of E.M.F. for potentiometer, (C) glass cell compartment containing diaphragm material (dimensions, diam. = 25 mm., height = 15 mm.), (D_1) drying tower containing $CaCl_2$, (D_2 and D_3) drying tube ($CaCl_2$) protecting liquid

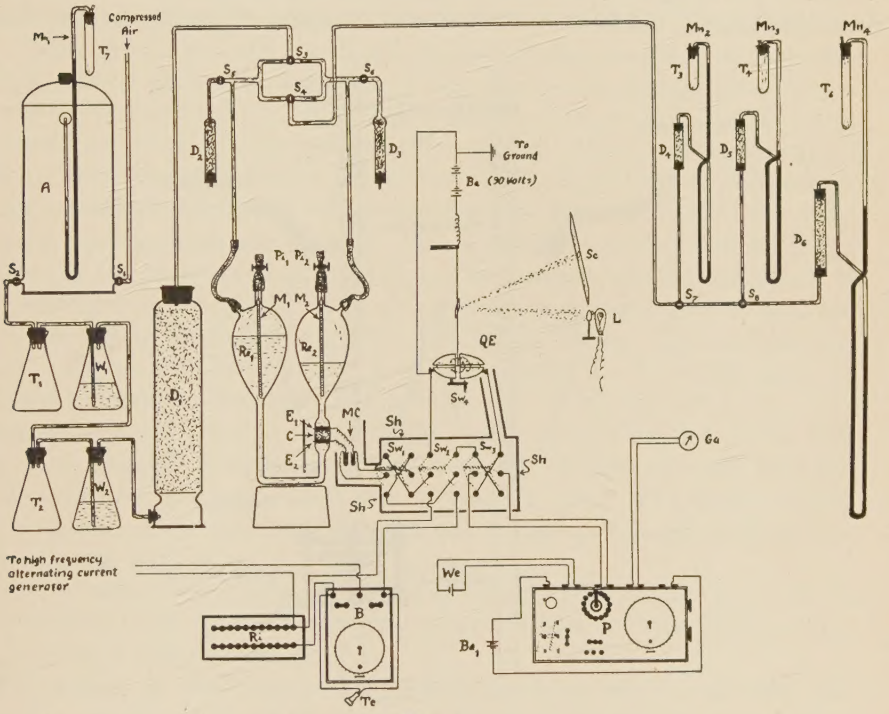


FIG. 1
Diagram of streaming-potential apparatus

system from atmospheric moisture, (D_4, D_5, and D_6) drying tubes ($CaCl_2$) in pressure line between manometers and liquid system, (E_1 and E_2) perforated gold (14 k.) electrodes one mm. in thickness and 30 mm. in diameter with platinum wire leads attached (perforations are 0.5 mm. in diameter and at as close intervals as possible without reducing mechanical strength of plate below that required to withstand operation of packing diaphragm), (Ga) galvanometer of moderate sensitivity used in balancing potentiometer, (L) lamp with housing and projection lenses which supplies beam of light to quadrant electrometer, (M_1 and M_2) cylindrical millimeter scales for measuring level of liquid in reservoirs Re_1 and Re_2 (consists of paper scale sealed in 5 mm. glass tube), (MC) mercury cups for making contact between streaming-cell and electrical measuring apparatus, (Mn_1) mercury manometer (900 mm.) indi-

cating pressure in compressed air tank, (Mn_2) water manometer (900 mm. = about 50 mm. Hg) for measuring pressure on liquid streaming through diaphragm (The water manometer being more than thirteen times as sensitive as the mercury manometer was used for systems giving high potentials under low pressures. Obviously, the pressures on such systems must be measured as accurately as possible in order to reduce error to a minimum.), (Mn_3) mercury manometer (900 mm.) used for measuring pressures on systems whose streaming-potentials are relatively low, (Mn_4) sulfuric acid manometer (1800 mm. = about 240 mm. Hg) used for measuring pressures on systems showing moderate potentials, *e.g.* 500 to 1000 millivolts at pressures of 200 to 240 mm. Hg,

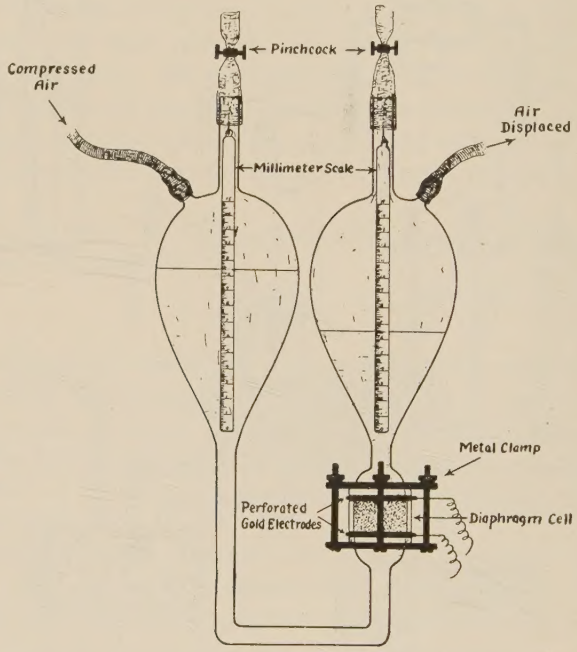


FIG. 2
Streaming-potential cell.

(P) potentiometer (L. and N. Type K), (Pi_1 and Pi_2) pinchcocks closing reservoirs Re_1 and Re_2, (QE) quadrant electrometer (Dolezalek type), (Re_1 and Re_2) reservoirs containing liquid streaming through diaphragm, (Ri) resistance used in conductivity measurements (Magnitude of resistance units range from 1 to 1,000,000 ohms.), (S_1) stopcock in compressed air line leading to tank A, (S_2) stopcock regulating the flow of compressed air from tank A into streaming-potential cell and manometer system), (S_3 and S_4) three-way stopcocks controlling the direction of flow of liquid through diaphragm, (S_5 and S_6) stopcocks connecting closed system with outer atmosphere through $CaCl_2$ drying tubes, (S_7 and S_8) three-way stopcocks in pressure line permitting the use of any one of the three manometers, or of balancing all three against one another for the purpose of determining the specific gravity

of the sulfuric acid or water relative to that of mercury), (Sc) ground-glass scale on which light beam from quadrant electrometer is projected, (Sh) shield of sheet copper protecting ungrounded side of circuit, (Sw_1) reversing switch which permits a reversal of the poles of the streaming cell, (Sw_2) double switch for connecting either the potentiometer or conductivity set, (Sw_3) reversing switch which permits a reversal of the poles of the potentiometer, (Sw_4) switch for "shorting" the quadrants of the electrometer, (T_1) trap between air tank and NaOH wash solution, (T_2) trap between NaOH wash solution in (W_1) and concentrated sulfuric acid in (W_2), (T_3, T_4, T_5, and T_6) safety traps for the contents of the manometers (Mn_1, Mn_2, Mn_3, and Mn_4 respectively) to catch the liquids in case pressure in the system is accidentally raised above the capacity of the manometer concerned, (Te) ear phones of conductivity set, (W_1) wash solution of 40 per cent NaOH which removes CO_2 from air in system, (W_2) drying solution of concentrated H_2SO_4, (We) Weston standard cell against which potentiometer is balanced.

Adjustment of Apparatus.—Having set up the apparatus as shown in the diagram, the quadrant electrometer (QE) is carefully leveled, and all of the switches of the entire system, except one (Sw_4) connecting the quadrants of the electrometer, are opened. The electrometer is next adjusted so that the needle is equally divided by the two pairs of quadrants. The positive terminal of the 90-volt battery (Ba) is then connected to the needle, and the negative terminal to one pair of quadrants. If the instrument is in proper adjustment, it will come to rest with the needle equally divided by the two pairs of quadrants. The beam of light from the electrometer will then fall on the scale (Sc) and its position may be taken as zero. The actual reading may be noted, or the scale may be adjusted so that its zero graduation coincides with the light beam.

The potentiometer (P) is, of course, adjusted by balancing the source of electromotive force against that of a standard cell, a suitable galvanometer being used as a null-instrument.

Preparation of Diaphragm.—Diaphragm materials were in all cases suspended in the liquid in which they were studied, for at least twenty-four hours before preparing the diaphragm, in order that sorption equilibrium might be established. The cellulose, which had been dispersed in the liquid by shaking, was packed into the cell (C) by the aid of suction and tamping with a glass rod. In all cases, except with liquids of high viscosity, the diaphragms were made as firm and close as possible.

Determination of Streaming-Potential.—The apparatus being in proper adjustment, the cell consisting of (Re_1), (Re_2), (C), (E_1), and (E_2) is assembled with the diaphragm described above, and the liquid to be studied poured into the reservoir (Re_1). The liquid is caused to flow from (Re_1) to (Re_2) through the diaphragm in (C) by turning stopcocks (S_3), (S_4), (S_5), and (S_6) so that compressed air, which has been dried by passing through concentrated sulfuric acid (W_2) and calcium chloride (D_1) and freed from carbon dioxide by bubbling through 40 per cent sodium hydroxide in (W_1), flows into the reservoir (Re_2). As the liquid flows from (Re_1) to (Re_2), air is displaced through

the tubulure in (Re_2), the stopcock (S_6), and the calcium chloride tube (D_3). When first assembled the diaphragm contains air bubbles, but upon streaming the liquid through it for a short time, the air is completely displaced.

To measure the difference in potential at the electrodes (E_1) and (E_2), the switches (Sw_1), (Sw_2), and (Sw_3) are closed so that the potentiometer is in circuit and the switch (Sw_4) is opened to disconnect the two pairs of quadrants of the electrometer. The potentiometer is then adjusted to deliver an electromotive force which will just balance the difference in potential between the electrodes (E_1) and (E_2). When these two electromotive forces exactly balance one another, the beam of light from the electrometer will come to rest at its zero point which has already been determined experimentally. Since the electromotive force varies with pressure, the potentiometer, the manometer, and the difference in level of liquid in (Re_1) and (Re_2) are all read in quick succession to avoid error due to change in pressure. The difference in level of the liquid in (Re_1) and (Re_2) is indicated by cylindrical glass millimeter scales (M_1) and (M_2), and a correction in pressure is calculated from the density of the liquid.

Determination of Specific Electrical Conductivity of Liquid in Diaphragm.—Having determined the streaming-potential at a series of pressures, the cell is connected to the conductivity apparatus by the switch (Sw_2) and the resistance of the diaphragm containing the streaming liquid is measured. The cell or "diaphragm constant" is determined by replacing the liquid in the diaphragm with N/10 potassium chloride. If the diaphragm liquid is insoluble in water, it is displaced with alcohol, and then by the standard potassium chloride solution. The specific conductivity of the liquid in the diaphragm is, of course, calculated from the cell constant and the observed resistance across the diaphragm containing the liquid.

Calculation of ζ-potential.—The numerical value for ζ-potential in electrostatic units is calculated from the formula, $\zeta = \frac{4\pi\eta H\kappa_s}{P\epsilon}$, by converting all of the values to c.g.s. units. In the simplest form, ζ volts $= 847{,}649{,}450 \times \frac{\eta H\kappa_s}{P\epsilon}$, where η = coefficient of viscosity, ϵ = dielectric constant, H = observed E.M.F. in volts, κ_s = observed specific conductivity of liquid in diaphragm in ohms^{-1}, and P = observed pressure in centimeters of mercury.

The sign of the potential may be either positive or negative depending upon whether one views the potential from the standpoint of the cellulose side or the liquid side of the double layer which exists at the interface. In the earlier work Briggs assigned a negative sign to the potential of a cellulose-water system, the *cellulose* being *negatively* charged with the corresponding positive charge in the liquid phase. We have followed this nomenclature in presenting our data.

Table I shows the values for the coefficient of viscosity, dielectric constant, and specific electrical conductivity used in the present series of experiments.

Diaphragm Material.—Cellulose.—A quantity of Schleicher and Schull filter paper No. 589 sufficient for the complete series of experiments was ground in a ball mill with 95 per cent ethanol until it was dispersed as completely as possible with a minimum of grinding of the fibers themselves. The cellulose was then filtered on a Büchner funnel, washed with absolute ethanol, dried *in vacuo* at 94°C. for 16 hours, and stored in sealed containers until used.

Liquids streamed through Diaphragms.—The following is a list of the liquids used in the streaming-potential measurements, together with their sources and methods of purification:

(1) Water: freshly redistilled water having a specific conductivity of 3 to 5 $\times$ 10^{-6} $ohms^{-1}$.

(2) Methanol: synthetic methanol distilled from alkaline solution to remove aldehydes, and then refluxed with an excess of anhydrous $CuSO_4$ to dehydrate, and subsequently redistilled.

(3) Ethanol: freshly prepared absolute ethanol (99.92 per cent).

(4) *n*-Propanol: (Eastman, C.P.)

(5) *iso*-Propanol: (Eastman, C.P.)

(6) *n*-Butanol: product of Industrial Solvents Company, redistilled. Boiling point = 116.5°C. to 117.0°C.

(7) *iso*-Butanol: (Eastman, C.P.)

(8) *n*-Hexanol: (Eastman, C.P.)

(9) *n*-Heptanol: (Eastman, C.P.)

(10) Ethylene glycol: (Eastman, C.P.)

(11) Glycerol: (Eastman, C.P.)

(12) Ethylene Chloride: (Eastman, C.P.)

(13) Ethylene Bromide: (Eastman, C.P.)

(14) Benzene: (C.P., thiophene-free)

(15) Chlorobenzene: (Eastman, C.P.)

(16) Bromobenzene: (Eastman, C.P.)

(17) Aminobenzene: freshly redistilled. Boiling point = 184°C. to 185°C.

(18) Methylbenzene: (C.P.)

(19) Nitrobenzene: Double redistilled. Boiling point = 209.5°C. to 210°C.

(20) Pinene: (Eastman, C.P.)

(21) *n*-Amyl Alcohol: (Eastman, Technical) Redistilled. Boiling point = 135.5°C. to 136.5°C.*

The Experimental Data.—(a) *Reproducibility of Results obtained with Different Diaphragms prepared from the same Sample of Cellulose.*—Since significant differences in experimental values depend upon the reproducibility of results by a given method, a number of determinations were repeated with the streaming-potential apparatus to ascertain the magnitude of variation

* Pure *n*-amyl alcohol has a boiling point of 137.8°C., while its isomers boil at from 102.5°C. to 127.8°C., hence the above is probably a mixture of isomeric forms.

TABLE I

Values for Constants used in the Calculation of ζ-Potential

(In the following table are given the values for (η) the coefficient of viscosity, (ϵ) the dielectric constant, and (κ_s) the specific electrical conductivity of liquid in diaphragm, used in calculating the ζ-potential values presented in all of the tables of experimental data.)

Table	System	η	ϵ	κ_s
	Cellulose in			
II A	Water	0.01	81.0	9.2811×10^{-6}
II B	Water	0.01	81.0	8.8608×10^{-6}
II C	Water	0.01	81.0	8.4267×10^{-6}
III A	Chlorobenzene	0.0077	5.610	3.8119×10^{-6}
III B	Chlorobenzene	0.0077	5.610	3.9070×10^{-6}
IV	Ethylene glycol	0.1733	41.2	1.3449×10^{-6}
V	Ethylene glycol	0.1733	41.2	1.2287×10^{-6}
VI	Water	0.01	81.0	8.8608×10^{-6}
VII	Methanol	0.0060	31.2	8.1439×10^{-6}
VIII	Ethanol	0.0119	25.8	7.5554×10^{-7}
IX	*n*-Propanol	0.0226	22.2	7.3665×10^{-7}
X	*iso*-Propanol	0.0222	26.0	9.9829×10^{-6}
XI	*n*-Butanol	0.0295	19.2	5.2885×10^{-6}
XII	*iso*-Butanol	0.0403	20.0	6.4535×10^{-7}
XIII	Ethylene chloride	0.0082	10.4	1.0581×10^{-6}
XIV	Methylbenzene	0.0058	2.378	5.0443×10^{-6}
	Chlorobenzene	0.0077	5.610	3.8119×10^{-6}
	Bromobenzene	0.0085	5.397	4.2011×10^{-6}
	Aminobenzene	0.0447	7.316	4.1202×10^{-6}
	Nitrobenzene	0.0183	36.45	5.1322×10^{-6}
XV	Ethylene bromide	0.0170	4.865	1.1559×10^{-6}
XVI	*n*-Hexanol	0.0451	14.3*	1.0743×10^{-5}
XVII	*n*-Heptanol	0.0701	12.2*	1.1988×10^{-5}
XVIII	Glycerol	8.30	56.2**	2.9392×10^{-6}
XIX	Pinene	0.0110	2.75	4.2602×10^{-6}
XX	Amyl alcohol (Tech.)	0.0454	16.0	8.8368×10^{-6}
XXII	Sucrose in *n*-Butanol	0.0295	19.2	1.8349×10^{-5}***

* Value for ϵ determined by extrapolation. ϵ for $CH_3OH = 31.2$, for $C_2H_5OH = 25.8$, for n-$C_3H_7OH = 22.2$, for n-$C_4H_9OH = 19.2$, and for n-$C_5H_{11}OH = 16.0$.

** Highest values given for ϵ in Landolt-Börnstein tables. Several values are given.

*** Values for κ obtained by displacing liquid in diaphragm with N/10 LiCl in *n*-butanol to obtain diaphragm constant.

due to experimental error which might be expected with the methods followed in the present investigation.

In Tables II and III are given the experimental results obtained by streaming water and chlorobenzene through different diaphragms prepared from the same sample of cellulose.

(b) *Effect of Pressure on the ζ-potential of Cellulose suspended in Ethylene Glycol for Four Hours and for Seventy-two Hours.*—A freshly prepared suspension of cellulose in ethylene glycol changes rapidly in physical properties with the progress of time. When first suspended in the liquid, the fibers appear opaque and quite distinct in outline, but in time they swell by taking up the liquid, become quite translucent, with a consequent increase in the viscosity of the suspension.

TABLE II

ζ-Potential of Cellulose-Water Interface as determined on Three Different Diaphragms prepared from the Same Sample of Cellulose

Pressure in mm. Hg	E.M.F. in millivolts	$\frac{\text{E.M.F.}}{P_{cm.}}$	ζ-Potential in millivolts
Diaphragm A[1]			
747.3	−391.2	−5.2347	−5.15
740.9	−386.2	−5.2127	−5.13
755.1	−393.0	−5.2044	−5.12
		Average =	−5.14
Diaphragm B[2]			
773.3	−470.2	−6.0804	−5.78
770.1	−472.6	−6.1369	−5.83
653.8	−408.5	−6.2481	−5.94
663.3	−402.1	−6.0621	−5.76
		Average =	−5.83
Diaphragm C[3]			
735.1	−423.4	−5.7597	−5.14
741.4	−427.4	−5.7651	−5.15
713.2	−420.2	−5.8914	−5.23
720.0	−422.2	−5.8637	−5.23
		Average =	−5.20

[1] $K_S = 9.2811 \times 10^{-6}$
[2] $K_S = 8.8608 \times 10^{-6}$
[3] $K_S = 8.4267 \times 10^{-6}$

As a preliminary study on the changes in the surface-electrical properties of the cellulose in different degrees of solvation, streaming-potential measurements at different pressures were made on two diaphragms, the cellulose of one being suspended in ethylene glycol for four hours and the other for seventy-two hours. The results secured are presented in Tables IV and V, and are shown graphically in Fig 3.

(c) *Effect of Pressure on ζ-potential.*—In the formula, $\zeta = \frac{4\pi\eta H K_S}{P\epsilon}$, it is assumed that E.M.F./P is a constant, and accordingly the values for ζ

determined for any liquid at different pressures will obviously also be a constant. To test the validity of this assumption, a series of both pure liquids

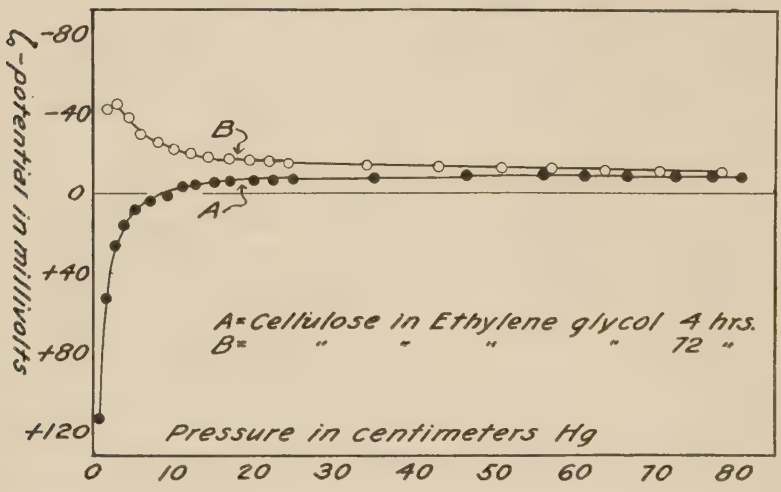


FIG. 3

Showing the ζ-potential effects of cellulose-ethylene glycol in relation to time and pressure.

TABLE III

ζ-Potential of Cellulose-Chlorobenzene Interface as determined on Two Different Diaphragms prepared from the Same Sample of Cellulose

Pressure in mm. Hg	E.M.F. in millivolts	$\frac{\text{E.M.F.}}{P_{cm.}}$	ζ-Potential in millivolts
Diaphragm A[1]			
781.5	−16.9	−0.2163	−0.99
776.5	−16.8	−0.2163	−0.99
771.8	−16.4	−0.2125	−0.97
787.9	−18.2	−0.2301	−1.05
783.9	−17.5	−0.2232	−1.02
778.6	−17.6	−0.2260	−1.03
		Average =	−1.01
Diaphragm B[2]			
782.0	−16.6	−0.2123	−0.94
798.6	−17.0	−0.2129	−0.95
795.6	−16.9	−0.2124	−0.94
790.9	−17.4	−0.2200	−0.98
803.9	−18.0	−0.2239	−1.00
800.1	−18.1	−0.2262	−1.01
794.8	−18.1	−0.2277	−1.01
797.7	−18.0	−0.2256	−1.00
		Average =	−0.98

[1] $K_s = 3.9070 \times 10^{-6}$
[2] $K_s = 3.8119 \times 10^{-6}$

and aqueous solutions were streamed through cellulose diaphragms at different pressures, and the streaming-potentials measured. The data for the pure liquids are given in Tables VI to XIII. We are omitting for the present the records of the data[10] secured when aqueous solutions were used, since these produced anomalous and as yet inexplicable effects. These effects are possibly due to selective adsorption at the cellulose-liquid interface of one of the components of the solution, and it seems probable that this selective ad-

TABLE IV

ζ-Potential of Cellulose suspended in Ethylene Glycol for Four Hours, in Relation to Pressure

Pressure in mm. Hg	E.M.F. in millivolts	$\frac{\text{E.M.F.}}{P_{cm.}}$	ζ-Potential in millivolts
9.5	+ 22.3	+23.57	+113.0
16.9	+ 18.7	+11.08	+ 53.1
27.5	+ 14.9	+ 5.41	+ 25.9
37.3	+ 12.5	+ 3.35	+ 16.1
51.5	+ 9.2	+ 1.79	+ 8.6
69.1	+ 5.7	+ 0.82	+ 4.0
92.0	+ 0.4	+ 0.04	+ 0.2
109.9	− 6.9	− 0.62	− 3.0
128.5	− 11.5	− 0.89	− 4.3
148.6	− 16.6	− 1.12	− 5.4
172.0	− 20.5	− 1.19	− 5.7
199.9	− 27.9	− 1.40	− 6.7
225.6	− 33.9	− 1.50	− 7.2
250.1	− 38.1	− 1.52	− 7.3
349.0	− 59.9	− 1.72	− 8.2
465.6	− 83.8	− 1.80	− 8.6
559.0	−101.1	− 1.81	− 8.7
612.1	−106.8	− 1.74	− 8.4
665.5	−117.2	− 1.76	− 8.4
725.0	−126.9	− 1.75	− 8.4
770.6	−134.9	− 1.75	− 8.4
806.1	−136.7	− 1.70	− 8.1
788.8	−133.7	− 1.70	− 8.1
776.2	−128.3	− 1.65	− 7.9
788.0	−129.7	− 1.65	− 7.9

[10] This record is on file in the Library of the University of Minnesota in the manuscript copy of the Ph.D. thesis of W. McK. Martin.

sorption (and subsequent desorption) is greatly influenced both by the pressure at which the liquid is streamed through the diaphragm and (possibly) by the electrification (which accompanies the streaming) of the interface.

The data in Tables VI to XIII demonstrate satisfactorily that the ζ-potential of cellulose in pure liquids approaches a constant value with increasing pressure. It is quite evident that the effect of pressure on the streaming-potential varies considerably according to the liquid bathing the cellulose fibers, and that in certain of the organic liquids the ζ-potential of cellulose does not approach a constant value until the pressure is raised to 700 or 800 mm. Therefore, it was decided to make all streaming-potential measurements at the highest pressures possible within the capacity of the apparatus; with systems giving low potentials, the pressure was maintained between 700 and 800 mm. However, with systems such as cellulose-*n*-butanol and cellulose-nitrobenzene, the capacity of the potentiometer (L. and N. Type K = 1.6 volts) prevented pressures of more than 200 mm. being used.

TABLE V

ζ-Potential of Cellulose suspended in Ethylene Glycol for Seventy-two Hours, in Relation to Pressure

Pressure in mm. Hg	E.M.F. in millivolts	$\frac{\text{E.M.F.}}{P_{cm.}}$	ζ-Potential in millivolts
18.4	− 17.8	− 9.66	−42.3
27.9	− 29.0	−10.39	−45.5
42.8	− 37.1	− 8.66	−38.0
59.2	− 40.9	− 6.91	−30.3
81.0	− 47.5	− 5.86	−25.7
99.2	− 51.4	− 5.18	−22.7
118.5	− 54.5	− 4.60	−20.2
143.7	− 59.5	− 4.14	−18.1
168.3	− 65.0	− 3.86	−16.9
196.1	− 72.8	− 3.71	−16.3
220.7	− 78.6	− 3.56	−15.6
244.9	− 83.3	− 3.40	−14.9
342.7	−105.4	− 3.07	−13.5
430.7	−126.0	− 2.92	−12.8
507.6	−144.2	− 2.84	−12.5
573.5	−157.9	− 2.75	−12.1
637.2	−170.6	− 2.68	−11.7
705.1	−184.8	− 2.62	−11.5
782.7	−196.9	− 2.51	−11.0

TABLE VI

ζ-Potential of Cellulose-Water Interface at Different Pressures

(The data are for a single diaphragm upon which readings were taken a various pressures in the order noted in the table.)

Pressure in mm. Hg	E.M.F. in millivolts	$\frac{\text{E.M.F.}}{P_{cm.}}$	ζ-Potential in millivolts
773.3	−470.2	−0.6080	−5.78
663.3	−402.1	−0.6062	−5.76
569.7	−345.1	−0.6058	−5.76
460.9	−279.1	−0.6056	−5.76
354.0	−210.9	−0.5958	−5.66
254.0	−144.9	−0.5705	−5.42
160.7	− 83.3	−0.5184	−4.92
69.4	− 15.0	−0.2161	−2.05
162.4	− 85.1	−0.5240	−4.98
254.1	−153.3	−0.6033	−5.73
356.0	−224.9	−0.6317	−6.00
452.3	−287.8	−0.6363	−6.05
553.1	−350.1	−0.6330	−6.02
653.8	−408.5	−0.6248	−5.94
770.1	−472.6	−0.6137	−5.83
798.4	−507.4	−0.6355	−6.04
765.1	−483.1	−0.6314	−6.00
549.5	−349.4	−0.6359	−6.04
355.1	−226.6	−0.6381	−6.06
150.4	− 87.6	−0.5824	−5.54

TABLE VII

ζ-Potential of Cellulose-Methanol Interface at Different Pressures

Pressure in mm. Hg	E.M.F. in millivolts	$\frac{\text{E.M.F.}}{P_{cm.}}$	ζ-Potential in millivolts
19.6	− 21.0	−10.70	−14.1
27.2	− 56.9	−20.94	−27.6
36.0	− 97.4	−27.02	−35.6
44.1	− 132.6	−30.07	−39.6
55.3	− 184.3	−33.34	−43.9
110.2	− 433.1	−39.29	−51.8
163.8	− 659.7	−40.29	−53.1
256.9	−1055.9	−41.11	−54.2
361.8	−1519.2	−41.99	−55.3

Table VIII

ζ-Potential of Cellulose-Ethanol Interface at Different Pressures

Pressure in mm. Hg	E.M.F. in millivolts	$\frac{\text{E.M.F.}}{P_{cm.}}$	ζ-Potential in millivolts
2.3	− 13.8	−60.53	−17.9
6.8	− 46.0	−67.35	−20.0
12.7	− 85.2	−67.03	−19.8
20.6	− 136.6	−66.41	−19.7
28.6	− 192.5	−67.19	−19.9
36.1	− 243.6	−67.46	−20.0
43.7	− 294.4	−67.43	−20.0
51.9	− 347.7	−67.01	−19.9
60.1	− 402.7	−67.02	−19.9
84.6	− 577.0	−67.17	−20.2
121.8	− 802.4	−65.90	−19.5
175.6	−1164.0	−66.28	−19.6
247.0	−1595.7	−64.61	−19.2

Table IX

ζ-Potential of Cellulose-*n*-Propanol Interface at Different Pressures

Pressure in mm. Hg	E.M.F. in millivolts	$\frac{\text{E.M.F.}}{P_{cm.}}$	ζ-Potential in millivolts
11.8	+ 39.8	+33.67	+21.4*
18.9	+ 59.5	+31.50	+20.0*
29.7	+ 84.5	+28.42	+18.0*
43.6	+115.0	+26.36	+16.7
60.4	+157.4	+26.08	+16.5
74.7	+192.3	+25.74	+16.3
87.8	+222.1	+25.28	+16.1
100.8	+258.4	+25.64	+16.3
116.2	+302.8	+26.05	+16.5
132.0	+348.6	+26.41	+16.8
146.7	+391.1	+26.66	+16.9
160.9	+433.0	+26.90	+17.1
175.4	+474.3	+27.03	+17.2
189.6	+513.3	+27.07	+17.2
206.0	+559.0	+27.13	+17.2
220.4	+600.9	+27.26	+17.3
237.5	+626.2	+26.36	+16.7
Average of all except *=			+16.8

Table X

ζ-Potential of Cellulose-*iso*-propanol Interface at Different Pressures

Pressure in mm. Hg	E.M.F. in millivolts	$\frac{\text{E.M.F.}}{P_{cm.}}$	ζ-Potential in millivolts
169.8	− 11.4	−0.67	− 4.8
267.9	− 35.0	−1.31	− 9.4
367.6	− 61.9	−1.68	−12.2
472.7	− 88.1	−1.86	−13.5
573.6	−115.2	−2.01	−14.5
672.7	−147.6	−2.19	−15.9
779.5	−175.1	−2.25	−16.2

Table XI

ζ-Potential of Cellulose-*n*-Butanol Interface at Different Pressures

Pressure in mm. Hg	E.M.F. in millivolts	$\frac{\text{E.M.F.}}{P_{cm.}}$	ζ-Potential in millivolts
17.1	+ 112.0	+65.61	+45.2
25.1	+ 172.6	+68.79	+47.4
32.5	+ 230.8	+71.04	+48.9
40.4	+ 290.8	+71.91	+49.5
48.3	+ 348.7	+72.25	+49.7
58.7	+ 425.0	+72.40	+49.8
73.2	+ 532.5	+72.74	+50.1
93.7	+ 686.2	+73.26	+50.4
112.8	+ 823.1	+72.99	+50.2
133.4	+ 990.0	+74.23	+51.1
156.7	+1181.2	+75.34	+51.9
191.8	+1441.0	+75.15	+51.7

TABLE XII

ζ-Potential of Cellulose-*iso*-butanol Interface at Different Pressures

Pressure in mm. Hg	E.M.F. in millivolts	$\frac{\text{E.M.F.}}{P_{cm.}}$	ζ-Potential in millivolts
23.8	+ 19.9	+ 8.38	+ 9.2
30.3	+ 31.3	+10.34	+11.4
44.4	+ 45.7	+10.28	+11.4
57.3	+ 59.2	+10.33	+11.4
67.9	+ 69.5	+10.23	+11.3
78.6	+ 83.2	+10.59	+11.7
91.7	+103.5	+11.29	+12.5
105.8	+124.6	+11.78	+13.00
118.2	+142.3	+12.04	+13.28
134.6	+163.8	+12.16	+13.42
152.1	+185.3	+12.18	+13.44
170.3	+204.4	+12.00	+13.24
192.3	+229.2	+11.92	+13.15
220.0	+260.9	+11.86	+13.08
243.1	+283.7	+11.67	+12.87
360.8	+421.5	+11.68	+12.89
503.4	+585.6	+11.63	+12.83
619.1	+712.7	+11.51	+12.70

TABLE XIII

ζ-Potential of Cellulose-Ethylene Chloride Interface at Different Pressures

Pressure in mm. Hg	E.M.F. in millivolts	$\frac{\text{E.M.F.}}{P_{cm.}}$	ζ-Potential in millivolts
21.0	− 49.4	−23.57	−16.64
35.2	− 85.2	−24.20	−17.08
66.4	−141.1	−21.24	−14.99
97.9	−218.6	−22.34	−15.76
132.1	−283.0	−21.42	−15.12
169.2	−362.4	−21.42	−15.12
194.8	−421.2	−21.62	−15.26
213.8	−472.8	−22.11	−15.61
		Average =	−15.70

In Tables XIV to XX inclusive, are presented the ζ-potential values obtained at approximately constant pressures. The averages from these tables and the values corresponding to those approaching a constant given in Tables II to XIII inclusive, are given in Table XXI.

TABLE XIV

ζ-Potential of Cellulose in Benzene and its Derivatives

Pressure in mm. Hg	E.M.F. in millivolts	$\frac{\text{E.M.F.}}{P_{cm.}}$	ζ-Potential in millivolts
A. Benzene			
0.0	0.0		0.0
800.0	0.0		0.0
B. Methylbenzene			
746.4	— 1.1	— 0.0147	— 0.15
754.5	— 1.2	— 0.0159	— 0.17
759.3	— 1.1	— 0.0145	— 0.15
756.8	— 1.1	— 0.0145	— 0.15
789.9	— 1.0	— 0.0126	— 0.13
779.8	— 1.1	— 0.0141	— 0.15
		Average =	— 0.15
C. Chlorobenzene			
782.0	— 16.6	— 0.2122	— 0.94
798.6	— 17.0	— 0.2128	— 0.95
795.6	— 16.9	— 0.2124	— 0.94
790.9	— 17.4	— 0.2200	— 0.98
803.9	— 18.0	— 0.2239	— 1.00
800.1	— 18.1	— 0.2262	— 1.01
794.8	— 18.1	— 0.2277	— 1.01
797.7	— 18.0	— 0.2256	— 1.00
		Average =	— 0.98
D. Bromobenzene			
775.0	— 90.6	— 1.1690	— 6.53
780.2	— 93.8	— 1.2022	— 6.71
787.2	— 93.7	— 1.1902	— 6.65
772.5	— 91.6	— 1.1858	— 6.62
796.6	— 96.7	— 1.2140	— 6.78
789.0	— 94.0	— 1.1914	— 6.65
		Average =	— 6.66
E. Aminobenzene			
764.6	— 178.1	— 2.3293	— 49.67
768.4	— 178.9	— 2.3282	— 49.65
766.2	— 178.4	— 2.3413	— 49.93
777.0	— 180.7	— 2.3255	— 49.59
790.8	— 183.6	— 2.3217	— 49.51
801.6	— 187.3	— 2.3366	— 49.83
		Average =	— 49.70
F. Nitrobenzene			
192.4	—1254.7	—65.21	—142.74
193.4	—1257.9	—65.03	—142.35
195.2	—1264.7	—64.79	—141.81
190.7	—1237.6	—64.90	—142.05
191.7	—1245.8	—64.99	—142.26
198.7	—1284.6	—64.66	—141.54
197.9	—1275.7	—64.46	—141.12
194.2	—1262.1	—65.00	—142.27
		Average =	—142.02

TABLE XV

ζ-Potential of Cellulose-Ethylene Bromide Interface

Pressure in mm. Hg	E.M.F. in millivolts	$\frac{\text{E.M.F.}}{P_{cm.}}$	ζ-Potential in millivolts
762.4	−230.4	−3.02	−10.36
764.1	−234.9	−3.07	−10.54
779.7	−244.7	−3.14	−10.76
792.7	−253.0	−3.19	−10.94
763.5	−248.6	−3.25	−11.14
750.9	−246.2	−3.28	−11.25
768.4	−253.5	−3.30	−11.31
772.1	−241.2	−3.12	−10.71
778.9	−248.1	−3.18	−10.92
779.5	−248.0	−3.18	−10.91
		Average =	−10.88

TABLE XVI

ζ-Potential of Cellulose-*n*-Hexanol Interface

Pressure in mm. Hg	E.M.F. in millivolts	$\frac{\text{E.M.F.}}{P_{cm.}}$	ζ-Potential in millivolts
690.1	+73.6	+1.0665	+30.63
712.1	+74.7	+1.0489	+30.13
726.4	+77.2	+1.0627	+30.52
759.7	+82.3	+1.0834	+31.11
754.8	+82.2	+1.0890	+31.27
785.8	+87.1	+1.1084	+31.83
714.2	+75.3	+1.0543	+30.28
723.3	+79.1	+1.0936	+31.41
751.5	+82.2	+1.0939	+31.41
775.7	+84.4	+1.0881	+31.25
762.9	+83.3	+1.0919	+31.36
		Average =	+31.02

TABLE XVII

ζ-Potential of Cellulose-*n*-Heptanol Interface

Pressure in mm. Hg	E.M.F. in millivolts	$\frac{\text{E.M.F.}}{P_{cm.}}$	ζ-Potential in millivolts
788.6	−7.8	−0.0989	−5.78
810.1	−8.2	−0.1012	−5.91
806.5	−8.0	−0.0992	−5.79
800.0	−7.9	−0.0988	−5.77
795.7	−7.8	−0.0980	−5.73
782.8	−7.6	−0.0971	−5.67
744.4	−7.4	−0.0994	−5.81
760.8	−7.6	−0.0999	−5.83
787.4	−7.8	−0.0991	−5.79
823.4	−8.0	−0.0972	−5.68
		Average =	−5.78

TABLE XVIII

ζ-Potential of Cellulose-Glycerol Interface

Pressure in mm. Hg	E.M.F. in millivolts	$\frac{\text{E.M.F.}}{P_{cm.}}$	ζ-Potential in millivolts
778.8	−23.9	−0.3069	−112.92
804.8	−24.4	−0.3032	−111.55
800.8	−24.3	−0.3034	−111.65
818.8	−24.7	−0.3016	−111.00
810.8	−24.5	−0.3022	−111.18
799.8	−24.0	−0.3001	−110.41
		Average =	−111.45

TABLE XIX

ζ-Potential of Cellulose-Pinene* Interface

Pressure in mm. Hg	E.M.F. in millivolts	$\frac{\text{E.M.F.}}{P_{cm.}}$	ζ-Potential in millivolts
768.8	−6.6	−0.0858	−1.24
789.8	−6.1	−0.0772	−1.12
784.6	−6.1	−0.0777	−1.13
779.9	−6.0	−0.0769	−1.12
710.7	−5.4	−0.0760	−1.10
749.1	−5.8	−0.0774	−1.12
759.5	−5.7	−0.0750	−1.09
777.7	−6.0	−0.0772	−1.12
		Average =	−1.13

* Eastman (practical)

TABLE XX

ζ-Potential of Cellulose in Amyl Alcohol*

Pressure in mm. Hg	E.M.F. in millivolts	$\frac{\text{E.M.F.}}{P_{cm.}}$	ζ-Potential in millivolts
749.3	+74.3	+0.9916	+21.06
744.2	+73.9	+0.9930	+21.09
740.4	+73.3	+0.9900	+21.03
730.0	+70.4	+0.9644	+20.49
761.3	+74.3	+0.9760	+20.73
754.0	+72.9	+0.9668	+20.54
754.0	+74.5	+0.9881	+20.99
747.4	+74.0	+0.9901	+21.03
		Average =	+20.87

* Redistilled Eastman (Tech.) *n*-amyl alcohol. Boiling point = 135.5 to 136.5°C. Boiling point of pure *n*-amyl alcohol = 137.8°C.. hence, above is probably a mixture of the isomeric forms.

ζ-Potential Sucrose-n-butanol Interface.—The studies on the surface-electrical properties of cellulose in the various pure organic liquids suggested the application of similar studies to another carbohydrate whose composition and structure were better known than are those of cellulose. While the cellulose used in these studies was probably of satisfactory purity, the molecular structure of such colloidal materials is uncertain, especially under different chemical environments. Certainly the degree of solvation of cellulose varies widely according to the nature of the liquid bathing its fibers.

Since considerably more is known about the chemical configuration of sucrose, it seemed of interest to measure the ζ-potential of sucrose crystals in some of the organic liquids in which it was relatively insoluble.

In making the streaming-potential measurements, practically the same procedure was followed as with the cellulose systems. The determination of the specific electrical conductivity of the liquid in the diaphragm of sugar crystals offered a difficulty, however, in that the "diaphragm constant" could not be determined by the use of a standard KCl solution on account of the solubility of the sucrose in aqueous solutions. This difficulty was overcome, however, by displacing the liquid in the diaphragm by a N/10 solution of LiCl in *n*-butanol to obtain the diaphragm constant. Having determined the specific electrical conductivity of N/10 LiCl in *n*-butanol and the resistance of the same solution in the diaphragm, the value for K_s was readily calculated.

TABLE XXI

Showing the Summary of the ζ-Potentials for Cellulose-Organic Liquid Interfaces, and the Electro-optical Constants for the Kerr Effect of the Same Liquids

	ζ-Potentials	The Electro-optical Constants of the Kerr Effect[1]		
	(Millivolts)	(2)	(3)	(4)
Water	− 5.4	*ca.* + 3.7		
Methanol	− 55.3	+ 1.11		
Ethanol	− 19.9	< + 0.78		
n-Propanol	+ 17.1	− 2.40	− 2.89	
n-Butanol	+ 51.7		− 4.19	
n-Hexanol	+ 31.0			
n-Heptanol	− 5.8		− 8.63	
iso-Propanol	− 16.2	+ 2.70		
iso-Butanol	+ 12.4	− 4.10	− 5.07	
Ethylene glycol	− 11.0			
Ethylene chloride	− 15.7		+ 6.70	+ 6.70
Ethylene bromide	− 10.9		+ 3.32	+ 3.28
Glycerol	−111.5			
Benzene	± 0.0	+ 0.46	+ 0.45	+ 0.418
Methyl benzene	− 0.2	+ 0.91	+ 0.90	+ 0.91
Chlorobenzene	− 1.0	+ 14.10	+ 14.26	+13.62 +13.80
Bromobenzene	− 6.7	+ 14.10	+ 13.85	
Aminobenzene	− 49.7		− 1.41	− 1.88
Nitrobenzene	−142.0	*ca.* +220.[5]	+372.97	+421.5
Pinene (Pract.)	− 1.1			
n-Amyl alcohol (Tech.)	+ 20.9			
n-(?) Amyl alcohol		−3.29		
iso-Amyl alcohol			− 3.64	
Tertiary amyl alcohol			+ 1.47	

[1] On the basis of B for $CS_2 = 3.70 \times 10^{-7}\lambda$ for $\lambda = 680$ mμ.
[2] Data of Schmidt[15]
[3] Data of Leiser[16]
[4] Data of Lippmann[17]
[5] Schmidt gives this figure as 22×10^2, but a recalculation of his data shows that the actual value is 220.

The electrical conductance of N/10 LiCl in *n*-butanol and ethanol is indicated by the following values:

$K_{n\text{-butanol}} = 2.2982 \times 10^{-6}$ ohms^{-1} (25.1°C.)

$K_{\text{N/10 LiCl in } n\text{-butanol}} = 2.0130 \times 10^{-4}$ ohms^{-1} (25.1°C.)

$K_{\text{Ethanol}} = 2.0599 \times 10^{-6}$ ohms^{-1} (25.1°C.)

$K_{\text{N/10 LiCl in ethanol}} = 1.4466 \times 10^{-3}$ ohms^{-1} (25.1°C.)

The solubility of sucrose in *n*-butanol appears to be very slight. The *n*-butanol used in these experiments was brought to equilibrium with the sucrose crystals by allowing the liquid to stand in contact with them, and shaking at intervals for 48 hours before making the streaming-potential measurements.

In calculating the ζ-potential values given in the following table, the values for η and ϵ of pure *n*-butanol were used. The amount of sucrose in solution was so small as not to appreciably alter the viscosity or dielectric constant. The electrokinetic potential at a sucrose-*n*-butanol interface is shown in Table XXII.

Surface Conductance of Cellulose in Water, Ethanol, and n-Butanol.— Briggs[5] observed that an aqueous suspension of cellulose was a better conductor of electricity than was pure water. This increase in conductivity was explained by Briggs as being due to the adsorbed layer of water molecules on the cellulose fibers having a higher conductance than the water in the continuous phase.

Although this aspect of the problem has not been studied in the present investigation, some conductivity values were obtained incidentally, which are of interest in connection with surface conductance in non-aqueous systems.

In the initial studies preparatory to the experiments on sucrose-*n*-butanol systems, the solubility and conductance of lithium chloride in pure ethanol and *n*-butanol were determined for the purpose of using these as standard solutions in obtaining the diaphragm constants.

The specific electrical conductivity of pure water, ethanol, and *n*-butanol, and the conductivity of the same liquids in cellulose diaphragms were as follows:

$$\kappa_{H_2O} = 4.8155 \times 10^{-6} \text{ ohms}^{-1}.$$

In tightly packed cellulose diaphragm, $\kappa_{s(H_2O)} = 8.4267 \times 10^{-6}$ ohms^{-1}.

TABLE XXII

ζ-Potential of Sucrose-*n*-butanol Interface

Pressure in mm. Hg	E.M.F. in millivolts	$\frac{\text{E.M.F.}}{P_{cm.}}$	ζ-Potential in millivolts
722.9	+40.3	+0.5574	+13.31
726.8	+41.1	+0.5655	+13.50
703.0	+40.2	+0.5718	+13.65
		Average =	+13.49

$\kappa_{n\text{-butanol}} = 2.2982 \times 10^{-6}$ ohm^{-1}.

In moderately packed cellulose diaghragm, $\kappa_{s(n\text{-butanol})} = 5.2885 \times 10^{-6}$ ohms^{-1}.

$\kappa_{\text{Ethanol}} = 2.0599 \times 10^{-6}$ ohms^{-1}.

In moderately packed cellulose diaphragm, $\kappa_{s(\text{ethanol})} = 7.5554 \times 10^{-6}$ ohms^{-1}.

In a diaphragm of sucrose crystals the values for *n*-butanol were: $\kappa_{n\text{-butanol}} = 2.2982 \times 10^{-6}$ ohms^{-1}.

In sucrose diaphragm, $\kappa_{s(n\text{-butanol})} = 1.8349 \times 10^{-5}$ ohms^{-1}.

Discussion

The initial experiments on the ζ-potential of cellulose-water and cellulose-chlorobenzene interfaces, the results of which are presented in Tables II and III show that it is possible to reproduce by use of the streaming-potential method, values which will check to within one millivolt.

Although one is probably not justified in using the combined results of a duplicate and a triplicate experiment as a basis for a generalization, the relative variation between the replicate values does indicate that different diaphragms prepared from the same samples of cellulose will yield comparable results.

These results confirm those of Briggs[5] in which he showed that the streaming-potential is not a function of relative porosity of the diaphragm, but rather a function of the pressure or the velocity of the liquid streaming through the diaphragm. This, however, is probably only true within certain limits, and such limits probably vary according to the chemical nature of the two phases bounding the interface.

The relation of streaming-potential to hydrostatic pressure or velocity of flow of liquid through the diaphragm as given in Tables VI to XIII inclusive, shows that when pure liquids were streamed through cellulose, the E.M.F. increased progressively with pressure, the value for ζ or E.M.F./P increasing from zero as a point of origin, and ultimately approaching a constant value.

In all of the systems studied, where a pure liquid was streamed through a cellulose diaphragm, there was but one exception to the above rule. In the one instance, however, that of ethylene glycol, the results of which are given in Tables IV and V, the values for ζ-potential decreased with increasing pressure and approached a constant value at pressures of about 800 mm. In the same experiment a diaphragm prepared from cellulose which had not reached an equilibrium with ethylene glycol, having been suspended in it for only four hours, gave a positive ζ-potential at low pressures, and gradually decreased to zero, and finally approached a constant negative value for ζ with progressively increasing pressures.

Since the cellulose showed very marked physical evidence of an increase in degree of solvation with increased time, the change in the "apparent" ζ-potential values calculated from the streaming-potential at low pressures, was probably due to surface-electrical disturbances caused by the changing conditions at the interface.

The data presented in Table XXI show very interestingly the relation of ζ-potential to molecular structure. When the homologues of the normal aliphatic alcohols are arranged in ascending order, the value for ζ progressively

changes, and up to the C_4 alcohol it is almost an inverse linear function of the number of carbon atoms in the chain. This relationship is shown graphically in Fig. 4.

The ζ-potential values in millivolts of the cellulose-liquid interface for the first four, the sixth, and the seventh alcohols of the series were as follows:

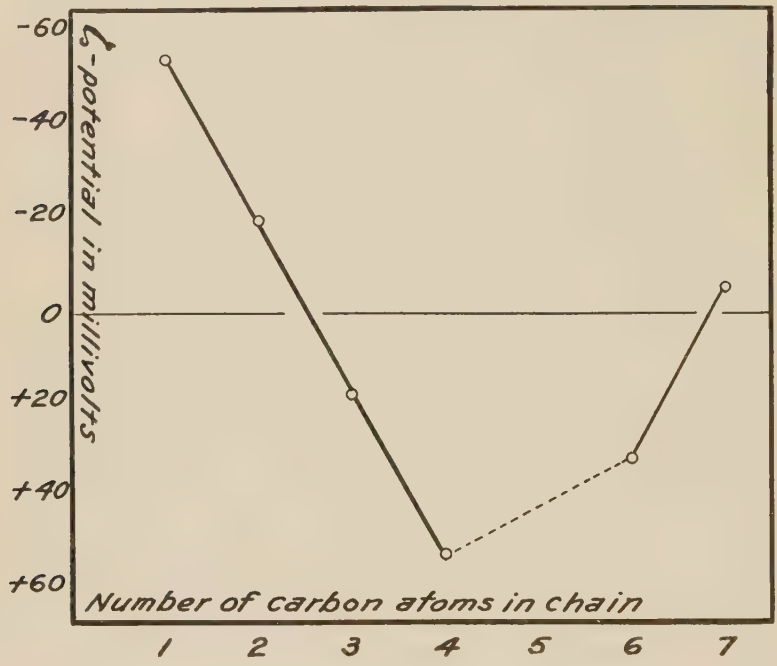


FIG. 4

Showing the relation of the ζ-potential at cellulose-*n*-alcohol interfaces as a function of the number of carbon atoms in the alcohols

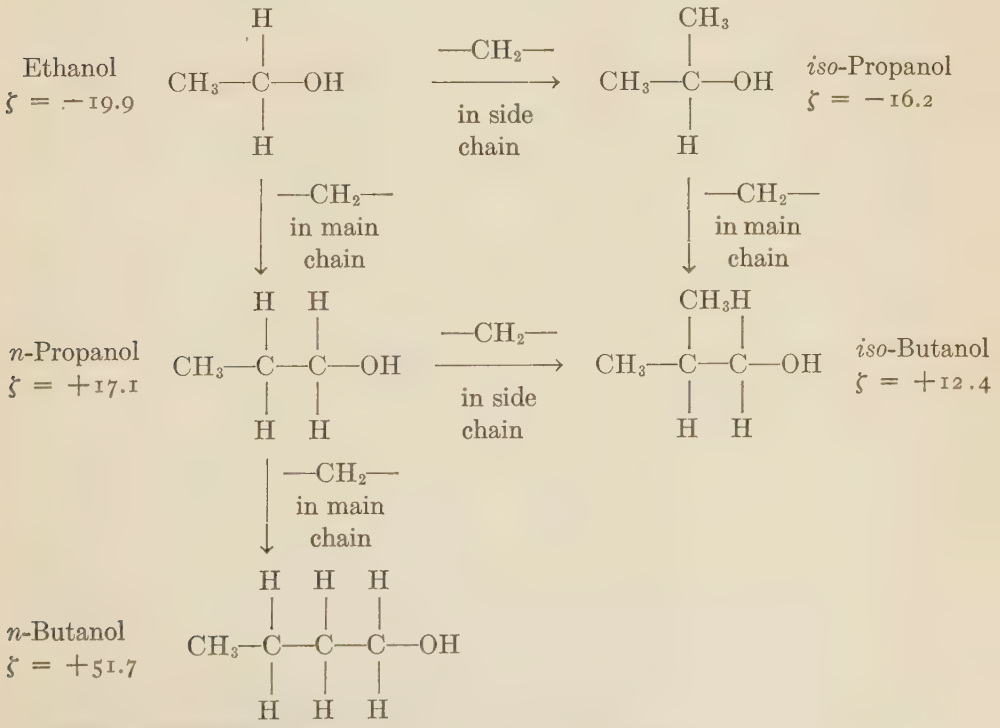
Alcohol	ζ-Potential	Difference due to one $-CH_2-$ group
Methanol	−55.3	
Ethanol	−19.9	35.4
n-Propanol	+17.1	37.0
n-Butanol	+51.7	34.6
n-Hexanol	+31.0	
n-Heptanol	− 5.8	36.8

Unfortunately, chemically pure *n*-pentanol could not be obtained in time to be included in these studies.

The relation of the ζ values of the C_6 and C_7 alcohols to the first four homologues may possibly be explained by assuming that the carbon chain is in the form of a spiral, the angle between each carbon atom being 109° in accordance with the regular tetrahedron concept of the valence forces (bonds) of the carbon atom. Since single-bond carbon atoms presumably rotate freely, a seven-carbon chain may assume an infinite number of configurations which range from that of a zigzag chain in a single plane to a three-dimensional

spiral. However, the structural configuration of the chain is probably such as to reduce its free electrical forces, and consequently its free energy, to a minimum. It follows that, if the molecule is dipolar, the two ends will attract one another and thus assume the spiral form. This viewpoint is supported by the recent paper of Lee and Van Rysselberge[11] who discuss the probabilities of a helicoidal arrangement of the carbon atoms in straight-chain carbon compounds. They point out that C_5, C_{10}, and C_{15} are characteristic points in many homologous series and that there is a corresponding periodicity in physical and chemical properties. "Multiples of C_5 (C_{10} and C_{15}) are related to C_5 itself in much the same way as the harmonies of a note are related to its fundamental. . . . "The pitch of the helix is such that if all of the C-atoms are arranged in two perpendicular planes, one complete turn of the helix has been made on reaching the 5th carbon atom." . . . "This periodicity is of fundamental importance in relation to the theory of chemical and interfacial actions, and, in general, ordinary physical properties also tend to a maximum or minimum at C_5, C_{10}, and C_{15}."

When the ζ values of the isomers are compared with those of their next lower normal homologues, it appears that the substitution of a methyl group for a hydrogen atom in the carbon chain lowers the ζ-potential by approximately 4 millivolts. The structural relationship of the isomers to their next lower homologues may be shown by writing their formulae in the following manner.



[11] Lee and Van Rysselberge: J. Phys. Chem., 33, 1543 (1929).

It is evident from a consideration of all the data that the electrokinetic potential of a solid-organic liquid interface is a function of the "unbalanced" polarity of the molecules bounding that interface, and that the molecular symmetry with respect to polar* and non-polar groups of the molecules which are oriented at the interface apparently determines the sign and magnitude of the potential difference across the interface.

That the ζ-potential is a function of molecular and polar symmetry is indicated by the values obtained for benzene and pinene. Both are hydrocarbons, but the former is symmetrical with respect to its three double bonds, while the one double bond of pinene renders it unsymmetrical. The ζ-potential of a cellulose-benzene interface was found to be zero, within the limits of error of our apparatus, while that of cellulose-pinene was -1.1 millivolts.

This hypothesis is still further supported by the data on the benzene derivatives. By substituting a methyl group for one of the hydrogen atoms in benzene, it showed a low but very definite negative potential of -0.2 millivolts.

That the electrokinetic potential across an interface is a function of the relative unbalanced polarity of the molecules oriented at that interface, is indicated by the ζ values obtained for the different substituents in the benzene ring. The values obtained for the following substituents were: -0.2 for methyl-, -1.0 for chloro-, -6.7 for bromo-, -49.7 for amino-, and -142.5 for the nitro-group. The unusually high potentials of the amino and nitro-groups are probably associated with the unsaturated valences of the atoms constituting these groups. Apparently the electrical forces (valence forces) of the N^{III} of the amino-group are not completely neutralized or compensated and consequently contribute to the electrokinetic potential. The unusually high value of -142.5 millivolts for the nitro-group is probably also due, in part at least, to the uncompensated or residual electrical forces of the double-bond oxygen atoms.

As the ζ-potential appears to reflect in a very definite manner the structural configuration of molecules, it offers promise of a wide application in the study of molecular structure and the nature of the molecular orientation present at interfaces. It may well be that it offers a means of quantitatively evaluating the relative "polarity" of molecules. Upon the same thesis, it may be used as a criterion of purity of chemical compounds.

Freundlich[12] has suggested that perhaps the electrokinetic potential effects which we have observed in these studies may be more or less closely related to the Kerr electro-optical effect. Kerr[13] observed that if the terminals of a Toepler-Holtz machine, or of a Leyden jar, or of an induction coil are imbedded in a block of glass placed between crossed Nicols and then a beam

* Polarity in this instance is taken to mean the relative free or residual valence or uncompensated electrical forces emanating from groups or atoms in combination with one another.

[12] Freundlich: Private communication.

[13] Kerr: Phil. Mag. (4) **50**, 335; **50**, 446 (1875); (5) **8**, 85; **8**, 229 (1879); (5) **9**, 157 (1880); (5) **13**, 153; **13**, 248 (1882).

of plane polarized light is passed through the glass perpendicular to the electrical field of force, the light has its velocity affected and is elliptically polarized, the maximum effect being observed when the plane of polarization makes a 45° angle with the lines of force of the electrical field. The effect of the elliptically polarized light was to cause the glass to become doubly refractive. The same phenomenon was shown by colophonium except that the effect upon the wave length of light was in the opposite direction, glass acting as a positive and colophonium as a negative crystal.

It was later found that many liquids showed the Kerr effect. Positive double refraction, similar to that of quartz, was shown by carbon disulfide, bromine, molten sulfur, etc., whereas many oils showed a negative double refraction analogous to that of Iceland spar.

This electro-optical phenomenon has been investigated by many workers, and Quincke[14] proposed the formula:

$$D = B\frac{P^2}{a^2}l$$

where D = the path difference measured in wave lengths of the light between the beams parallel and perpendicular to the lines of force of the electrical field, P = the potential (in absolute electrostatic units) of the electrical field, l = the length in cm. of the fluid column illuminated by the light, a = the thickness in cm. of the illuminated layer of liquid, B = an *electro-optical constant* which is a characteristic constant for the liquid or substance being investigated.

Schmidt,[15] Leiser,[16] and Lippmann[17] in particular have determined the Kerr electro-optical constant for a large series of organic compounds. Their data include most of the liquids which we have used, and their electro-optical constants are appended to our data in Table XXI. It will be noted that there is a striking parallelism between the ζ-potential data and the electro-optical constants. This is particularly true as to the sign* of the ζ-potential and the electro-optical constant, only two reversals of sign appearing, *i.e.*, *n*-heptanol and aniline. Aniline presents by far the most striking divergence. Perhaps it is too much to expect an absolute parallelism in such divergent physical measurements. It is striking to note, however, that the break in sign in the series of *normal* alcohols comes in both instances between ethanol and propanol and that nitrobenzene produces in both series of data by far the greatest effects.

Kerr himself ascribed the electro-optical effect to an orientation of the molecules in the substance under test. Thus he states, "No theoretical con-

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[14] Quincke: Wied. Ann., **19**, 729 (1883).

[15] Schmidt: Diss. Göttingen (1901); Ann. Physik (4) **7**, 142 (1902).

[16] Leiser: "Elektrische Doppelbrechung der Kohlenstoffverbindungen." Habilitationsschr. Karlsruhe (1910). Cited at length by Lippmann (original not seen).

[17] Lippmann: "Elektrische Doppelbrechung in Flüssigkeiten und ihre Beziehung zu chemischer Zusammensetzung und Konstitution." Inaug.-Diss. Leipzig (1912) 172 pp.

* It should be remembered that the electro-optical constant is for the liquid phase and that the signs of the electrokinetic potential would be reversed if the sign designated the charge on the liquid phase.

ception can present itself more naturally than that of an induced structure, a regular arrangement of polarized molecules roughly illustrated by the common 'magnetic curves'." Later physicists[18] suggested that the effect might be due to a change in the vibration frequency of the electrons. However, Leiser concluded that the molecules of the liquid assumed a definite orientation in the electrical field and that this orientation of the molecules caused the double refraction. This view is strongly supported by Lippmann's observations, particularly in those systems where he was working with known mixtures of two liquids, in which systems definite maximum electro-optical effects were observed at certain molecular concentrations.

We have ascribed the electrokinetic effects which we observed to an orientation of the molecules of the liquid phase at the cellulose-liquid interface so that in this respect at least the two phenomena appear to be on common ground. Whether or not the electrical potential produced by the streaming is sufficiently high to produce a molecular orientation, such as induces the Kerr effect, in the body of the liquid is problematical, but such a possibility cannot be entirely ruled out. Both Leiser and Lippmann observe that no other physical property of organic compounds shows such extreme variations in magnitude as does the electro-optical constant. To this observation we must add that the electrokinetic potential effects are of a similar order of magnitude.

Summary

The ζ-potentials of cellulose-liquid interfaces involving nineteen pure organic liquids have been determined by a streaming-potential method. The data support the following conclusions:

1. Studies of the factors influencing streaming-potential measurements have shown that with cellulose-organic liquid interfaces the ratio of E.M.F./P for pure liquids arises at zero and approaches a constant value with progressively increasing pressures.

2. The ζ-potential at a cellulose-organic liquid interface is a function of the structure of the molecules oriented at the interface, and the relative symmetry of the molecules with respect to polar groups or double bonds determines the sign and magnitude of the potential.

3. In an homologous series of the *n*-aliphatic alcohols, a $-CH_2$-group in the chain alters the ζ-potential by approximately $\pm$ 36 millivolts, whereas the substitution of a methyl group for a hydrogen atom to form a branched-chain alcohol alters the ζ-potential by only ± 4 millivolts.

4. The data support the theory of a helicoidal configuration of the carbon atoms in an homologous series of the *n*-aliphatic alcohols.

5. In the benzene series the symmetrical hydrocarbon, C_6H_6, produced no measurable ζ-potential when streamed through a cellulose membrane; the somewhat unsymmetrical but non-polar methyl benzene produced a low

[18] See historical of Lippmann.

but measurable potential; and the highly polar and unsymmetrical nitrobenzene induced the highest potential of all compounds which were investigated.

6. When various groups were substituted for hydrogen in the benzene molecule, the electrokinetic effect follows the order, $H < CH_3 < Cl < Br < NH_2 < NO_2$.

7. Although no absolute parallelism exists, there is a striking similarity between the electrokinetic potential at a cellulose-organic liquid interface and the Kerr electro-optical constant which is a characteristic of the organic liquid.

8. Since the ζ-potential is a function of molecular structure, the streaming-potential method may be used advantageously in studies dealing with the structural configuration of molecules. The ζ-potential values may also be used as a criterion of purity of chemical compounds.

VITA

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Publications

The Extraction of Leaf-Tissue Fluids and Their Utility in Physiological Studies (with R. Newton and W. R. Brown). *Plant Physiology*, 1:57-65. 1926.

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Honor Societies: Gamma Alpha and Sigma Xi.

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